COATINGS AND ENAMELS

MUTUAL INFLUENCE OF THE COMPONENTS OF WHITE SINGLE-LAYER GLASS ENAMELS ON THE OPACIFICATION MECHANISM

E. A. Yatsenko[1]

Questions concerning the mutual influence of the components of enamel on the degree its opacification are examined. Experimental results, which are generalized taking account of previously obtained data, are presented.

Key words: single-layer glass enamel coating, mechanisms of opacification, crystallization, lithium titanate, cubic structure.

The requirements imposed on the quality of enameled articles are largely predetermined by the structure of the glass coating itself as well as by the metal – enamel composition formed. For this reason, to solve the technological questions successfully it is necessary to investigate the structure as well as the physical – chemical processes occurring when an enameled article is fired. In so doing, it is important to study not only the individual components of a composition but also their interaction during firing in the contact-metamorphic zone.

In our previous investigations [1, 2] we obtained inorganic heterogeneous coatings consisting of a continuous glassy matrix and dispersed crystalline oxide particles, separating as a result of the crystallization of the melt. It was shown that it is possible to obtain different low-melting white coatings in a wide range of technological and operational properties by varying the ratio of the matrix and dispersed phases. Our objective in the present work is to study the mechanism of opacification of white single-layer enamels for steel.

Fluorine containing compounds, despite their positive effect on the properties of glasses (decrease of viscosity during founding, opacification capability, and so forth) were excluded from the mix because of their toxicity. Alkali-earth oxides were also excluded from the glass composition to increase fusibility. Since the coatings developed must be single-layered and give a white color in a thin layer, TiO_2 was

used for effective opacification. In addition, it is known that the degree of crystallization of the glass depends on the temperature – time conditions for heat-treatment of the glass. In our case they must be as close as possible to the process conditions for depositing enamels.

Figure 1 displays a fragment of the pseudo-ternary system $R_2O – TiO_2 – (B_2O_3 + SiO_2)$, where R = Li, Na, K, in which glass with the required properties, specifically, glassmaking temperature no higher than 1200°C, firing temperature no more than 720°C, uniform crystallization over the entire volume giving whiteness at least 75%, and luster not less than 70%, were sought.
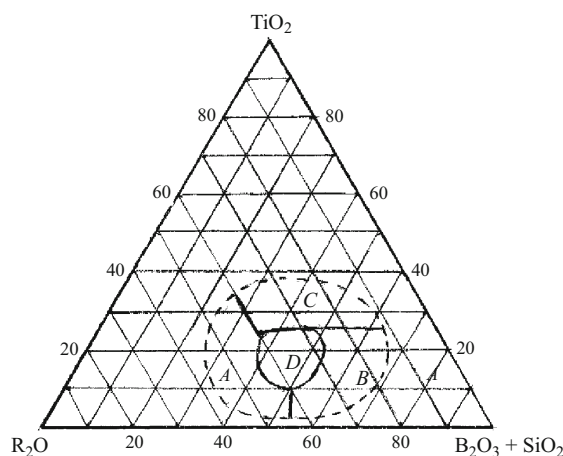

Fig. 1. Fragment of the pseudo-ternary system $R_2O – TiO_2 – (B_2O_3 + SiO_2)$.

[1] Southern Russia State Technical University, Novocherkassk, Russia (E-mail: e yatsenko@mail.ru).

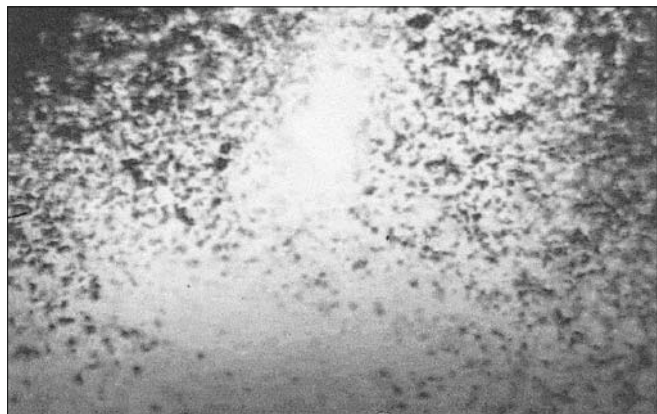**Fig. 2.** Photomicrograph of a sample of crystallized glass in reflected light ($\times$ 320).
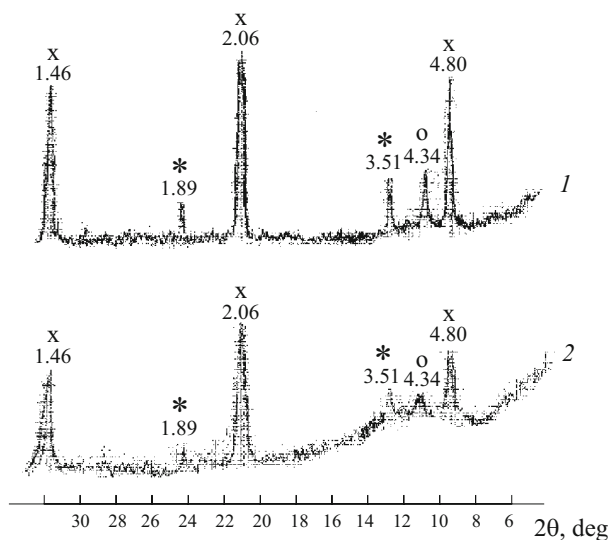

Fig. 4. Photomicrograph of an immersion preparation of glass in transmitted light ($\times$ 500): *1*) glass; *2*) titanium dioxide; *3*) lithium titanate.

Fig. 3. Diffraction patterns of samples of heat-treated glasses with compositions lying in the regions *B* (*1*) and *C* (*2*): $\times$) Li_2TiO_3; $\bigcirc$) Na_2SiO_3; $\ast$) TiO_2.

It was found that active opacification of glass occurs in the regions *B* and *C* of the system $R_2O - B_2O_3 - SiO_2$. Complete crystallization of glass with formation of a lusterless matte surface is observed in the region *B*. In region *C* partial volume crystallization is observed, glasses are well opacified and have high brightness and luster.

Figure 2 displays a photomicrograph in reflected light of the surface of a sample of crystallized region-*C* glass on which a fine-crystalline phase can be seen.

X-ray phase and crystallographic analyses were performed to determine the character of the crystallization of the glasses in the composition range studied. XPA shows the crystalline phase in all samples with compositions in the regions *B* and *C* to be lithium titanate Li_2TiO_3 (Fig. 3). This is explained by the fact that in the indicated ranges more alkali oxides are present than in the region *A*. For a set constant ra-
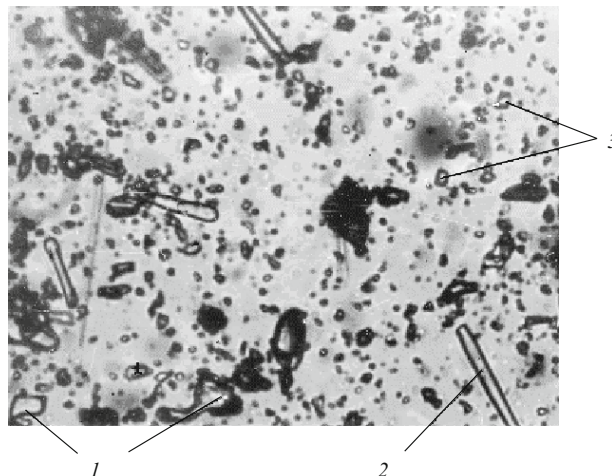
tio of the alkali oxides (1.0 : 0.4 : 1.0%[2]) the glass samples in these regions are enriched with Li_2O, whose content ranges from 18 to 21%. The Li^+ ion (in contrast to Na^+ and K^+), possessing a small ionic radius (r_{Li^+} = 0.68 Å [3]) and,

because of its strong force field, holding its oxygen more strongly, i.e., it plays a special role in glass, actively promoting liquation and crystallization. The ratio $Li_2O : TiO_2$ in the regions *B* and *C* is higher than in the region *A*.

Together with Li_2TiO_3 the diffraction patters show weak maxima of other crystalline phases, specifically, sodium silicate Na_2SiO_3 and TiO_2 in a low-temperature modification (anatase). Crystallization is essentially complete in the region *B* — strong reflections of the phase Li_2TiO_3 are observed, and less intense reflections against the background of a stronger amorphous halo due to a glass are observed in the region *C*, where the reflections of the crystalline phase are weaker.

The crystal-optical methods of analysis confirm these data. Specifically, the immersion method established that the main phase (Li_2TiO_3) possesses a high index of refraction n_{av} = 2.07 (measured to within $\pm$ 0.02 using selenium and sulfur alloys), the crystals are not birefringent and have an isometric form, i.e., they are cubic (Fig. 4). Together with Li_2TiO_3, birefringent crystals with a higher refractive index n_g = 2.53 and n_p = 2.47 are encountered but in much smaller quantities. The latter are probably anatase; $n \sim 1.550$ for the glass phase (measured using immersion liquids to within $\pm$ 0.005).

Crystallization of Li_2TiO_3 is atypical for multicomponent glasses; we are the first investigators to establish this. Different opinions exist concerning the character of Li_2TiO_3 crystallization in the system $Li_2O - TiO_2$. The crystalline structure of Li_2TiO_3 depends on the conditions under which the

---

2 Here and below — the molar content, unless specially stipulated.

compounds are obtained. There are two known modifications of Li_2TiO_3: high-temperature cubic of the NaCl type, which exists at temperatures above 1150°C ($a = 8.28$ Å), and low-temperature monoclinic, which is a derivative of the NaCl cubic structure. However, for synthesis with an oxygen deficiency (1 mm Hg) the cubic modification can be obtained at low (600 – 800°C) temperatures.

A cubic modification was also obtained at temperature 600°C from the solution $Li_2[TiO(C_2O_4)]$ by the heat-shock method. Subsequent heating gives an improved structure; lines due to a transition into the monoclinic modification appear at higher temperatures (950°C), and at 1050°C the latter modification transforms once again into the cubic modification. Other data show that Li_2TiO_3 forms a wide range of solid solutions at temperatures above 1215°C. These solutions have a disordered NaCl-type cubic structure. At lower temperatures the structure is ordered monoclinic. The cubic solid solutions range from 42 to 65% Li_2O at 1295°C. Away from stoichiometry the region of cubic solid solutions based on Li_2TiO_3 extends in the direction of low temperatures, down to 955°C [4].

Thus, the Li_2TiO_3 phase departs substantially from stoichiometry.

In addition, a study of the conductivity of lithium titanate with the composition $Li_4Ti_5O_{12}$ established that the low-temperature modification of this compound with the structure of spinel at temperature about 530°C transforms into a high-temperature modification with a disordered NaCl structure under the ordinary conditions. All this shows that the region of existence of the high-temperature disordered modification of Li_2TiO_3 is much wider and extends in the direction of increasing content of titanium dioxide and decreasing temperature. In addition, the symmetry of a Li_2TiO_3 cell depends strongly on the formation conditions, i.e., a cubic modification of Li_2TiO_3 can be obtained even at 600°C.

Under our enamel-deposition conditions at temperatures 680 – 720°C with 6-min soaking and cooling at the rate 50 – 80 K/min these crystals can form from melt and grow (i.e. the mechanism is the same as when crystals are grown from a fluxed solution). Thus, it is evident that in a melt of enamel with a complex composition the Li_2TiO_3 phase can crystallize, on cooling, into the cubic modification at a much lower temperature, which is in fact observed in the present experiment.

It is known that phases with a completely disordered structure possess low formation energy and can crystallize easily. The crystallization of Li_2TiO_3 can be explained from the structural standpoint. This phase posses a NaCl-type cubic structure (general formula AB) of the closest-packing type where the Li^+ and Ti^{4+} ions are distributed randomly over the octahedral positions A. As a result, it possesses a wide range of homogeneity, which promotes its crystallization even with a large departure from stoichiometry. At the same time the crystalline phases with lower symmetry, specifically, phases in the form of anatase TiO_2 (weak reflec-

tions with $d = 3.51$, 1.89 Å) and Na_2SiO_3 ($d = 4.34$ Å) are formed in negligible amounts.

It is well known that Ti^{4+} can be found in various crystalline compounds, including in glass, in two coordination states — octahedral and tetrahedral. In silicate glasses Ti^{4+} can replace Si^{4+} (coordination number CN = 4) isomorphically and become incorporated in the glass network as well as play the role of modifying cation with CN = 6. XPA shows that crystalline phases are not seen in the composition ranges A and C (transparent glasses annealed at 1200 – 1300°C), while the IR spectroscopy showed strong absorption bands in the region 740 – 780°C, which correspond to vibrations of the Ti – O bonds of quadruply coordinated Ti^{4+}, and at the same time strong absorption bands appear in the [TiO_6] region — 500 – 600 or 500 – 700 cm^{-1}, corresponding to the vibrations of Ti – O bonds (CN $Ti^{4+} = 6$). On the other hand, there is only one band in the IR spectra of samples of crystallized glasses from the regions B and C — 550 – 570 cm^{-1}, indicating the CN = 6 for titanium, which agrees with the XPA data on the crystallization of Li_2TiO_3.

Titanium dioxide is an opacifier in silicate and borosilicate enamels. As a rule, opacification in the systems Me_2O – TiO_2 – SiO_2 – B_2O_3 (Me = Li, Na, K) is due to the crystallization of TiO_2, whose minimum amount depends on the content of the other components of the system. Our systems have six components. Thus far such systems have been little studied, although multicomponent glasses are widely used, including for the fabrication of coatings. Some of the most widely studied systems are four-component titanium-containing aluminosilicate, sodium-borosilicate, and sodium-titanium-borosilicate glasses. In the latter the region of glass formation is small and extends to composition with 25% TiO_2. The degree to which TiO_2 becomes incorporated into the glass network increases as the system passes from high-boron to high-silica properties.

This pattern remains as the Na_2O content increases, the amount of TiO_2 in the glasses increasing at the same time. This behavior is also characteristic for the multicomponent systems Al – Si with TiO_2 added. However, in complete accord with the general laws of glass formation an increase in the number of components results in an expansion in them of the regions of stable glass as a result of both a decrease of the melting temperature and the suppression of crystallization and liquation of the melts.

In our case, because of the multicomponent nature of the system and, apparently, the simultaneous presence of three alkali oxides as well as the low melting temperatures of the compositions and rapid cooling of the melt Li_2TiO_3 forms as a phase that precipitates on crystallization. It is known that in ternary titanium-silicate glasses, in the presence of MeO and Me_2O, which introduce easily polarized ions of oxygen, titanium forms with high probability octahedral complexes of the type $[TiO_{6/2}]^{-2}Me_2^+$ [6] and in our case, where Na^+, K^+, and Li^+ are present simultaneously, octahedral complexes of

the type $[TiO_{6/2}]^{-2}Li_2^+$. The latter form nuclei of the Li_2TiO_3 phase on phosphate centers of crystallization.

It is known that liquation occurs in the three- and four-component titanium-containing systems. In our case liquation is not observed for the selected regime of heat-treatment and cooling of the enamel. It can be conjectured that rapid crystallization results in the presence of centers of crystallization containing phosphorus. Prolonged anneals of glass (from 10 min to 1 h at 550 and 600°C) from region *A*, where crystallization was not observed in glass obtained in the standard regime were performed to moderate opacification. Well-opacified glasses were obtained only with prolonged soaking (from 1 to 2 h), which is undesirable for the present enameling technology.

Transparent glasses (region *A*) are formed with lower Li : Ti ratios, while the Na : Ti and K : Ti ratios remain high, which confirms the well-known fact that alkali-metal oxides with large cations have a positive effect on the incorporation of Ti into the glass network because of the coordination number changing from 6 to 4. If there are no centers of crystallization, then Li_2TiO_3 crystallization is too slow and slow cooling is required.

The influence of small additions on the crystallization of glasses is well known. Thus, the laws governing the effect of small additions of the oxides of group I – VIII elements in the sitilization of glass in aluminosilicate systems of the type $MeO(Me_2O) – Al_2O_3 – SiO_2 – TiO_2$ (Me — MgO, Me_2O – Li_2O, Na_2O) have been investigated. It has been established that small (to 1.5%) additions of oxides do not change the composition of the main crystalline phases but they do increase their content, intensifying the crystallization process. As the concentration of additives increases, their individual properties become evident, i.e., they too can form crystalline phases, thereby decreasing the content of the main crystalline phase, and change the course of phase transformations.

In these system, additions of B_2O_3, P_2O_5, SnO_2, Nb_2O_5, and Ta_2O_5 intensify the separation of rutile both directly from the glass and by means of acceleration of the decomposition of aluminum titanate in the system $Li_2O – Al_2O_3 – SiO_2 – TiO_2$. The incorporation of impurity cations into the glass structure and the appearance of defective sections with nonequivalent bonds could be responsible for the observed intensification of the precipitation of crystalline phases as well as for their stabilization and decomposition. The effect of small additions is related with the difficulty of intrinsic formation of the phases with glass components, on the one hand, and the difficulty of their incorporation into the glass framework on the other hand.

Small additions of oxides in glasses create centers of crystallization. As a rule, crystallization of this type is fast and does not require additional prolonged heat-treatment. Our glass compositions contain as small additions Al_2O_3 and P_2O_5 in amounts 2 wt.% (molar content is about 0.8%).

To clarify the possibility of creating centers of crystallization with these oxides we performed a series of experiments to determine the dependence of the degree of opacification on their content with a constant ratio of the concentrations of all other components. It was determined that changing the mass content of Al_2O_3 from 0.5 to 5.0% keeping the P_2O_5 mass content constant and equal to 2% has virtually no effect on the intensity of the opacification of glass, since the whiteness and luster do not change much and are in the following ranges: luster — 45 – 50% and whiteness — 80 – 85%. Therefore it can be supposed that it is P_2O_5 that forms the phosphorus-containing microregions that result in the appearance of centers of crystallization where Li_2TiO_3 crystallizes actively.

In summary, it was determined that the components of glasses have a mutual effect on the mechanism of opacification of white single-layer enamels.

REFERENCES

1. E. A. Yatsenko, A. P. Zubekhin, and E. B. Klimenko, "Resource-conserving technology of protective coatings for steel based on aluminum-containing waste," *Praktika Protivokor. Zashchity*, No. 1, 13 – 15 (2002).
2. E. A. Yatsenko, A. V. Ryabova, A. P. Zubekhin, and V. A. Guzii, "Single-layer low-melting white glass enamel coatings for household gas appliances," *Steklo Keram.*, No. 1, 29 – 30 (1997); E. A. Yatsenko, A. V. Ryabova, A. P. Zubekhin, and V. A. Guzii, "One-coat low-melting point white vitreous enamels for household gas appliances," *Glass Ceram.*, **54**(1 – 2), 30 – 31 (1997).
3. R. D. Shanon and C. T. Prewit, "Effective ionic radii in oxides and fluorides," *Acta Cryst.*, **25**(5), 925 – 958 (1969).
4. *Handbook of Phase Diagrams of Systems of Refractory Oxides, Issue No. 5, Binary Systems, Part 1* [in Russian], Nauka, Leningrad (1985).
5. I. A. Leonidov, O. N. Leonidova, L. A. Perelyaeva, et al., "Structure, ionic conductivity, and phase transformations of lithium titanate $Li_4Ti_5O_{12}$," *Fiz. Tverd. Tela*, **45**(11), 2079 – 2984 (2003).
6. R. Ya. Khodakovskaya, *Chemistty of Titanium-Containing Glasses and Sitals* [in Russian], Khimiya, Moscow (1978).